Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fluorine-free organic electrolytes for the stable electrodeposition of neodymium metal

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Electronic Supplementary Information (ESI)

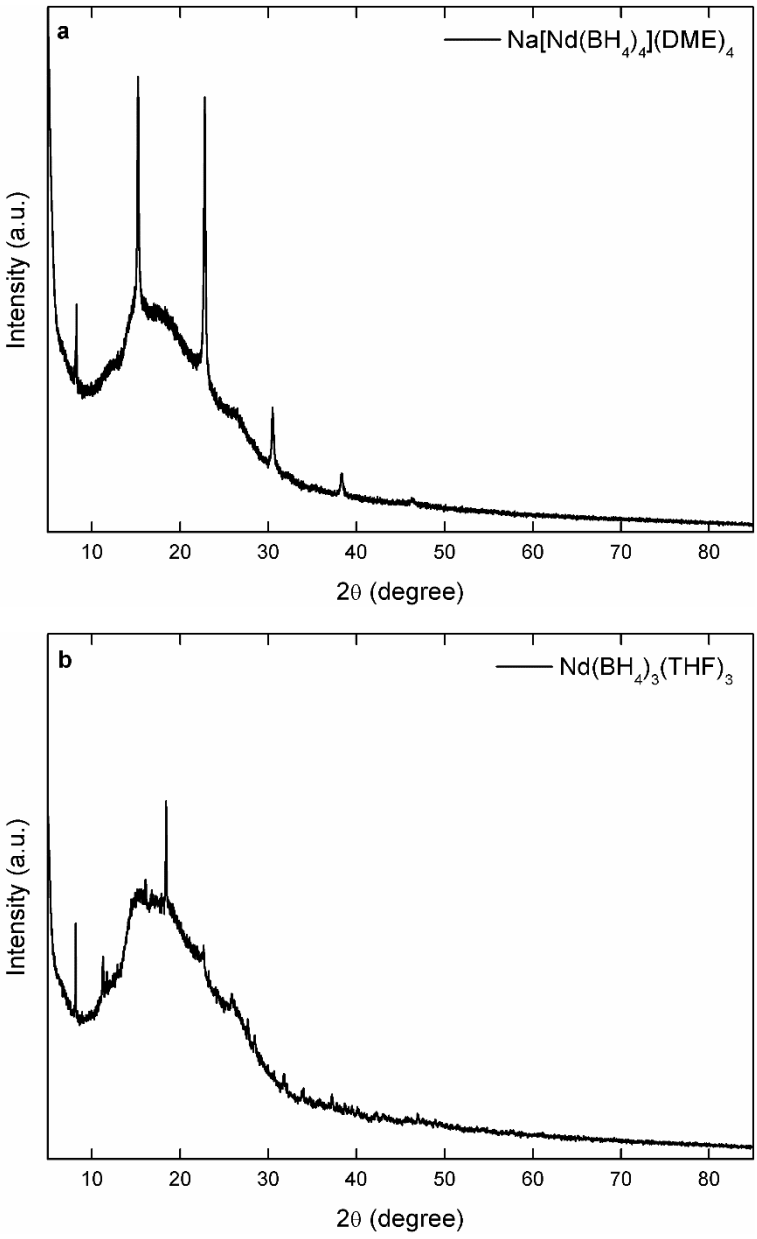

Figure S1. Powder XRD diffractograms of the complexes $Na[Nd(BH_4)_4](DME)_4$ (a) and $Nd(BH_4)_3(THF)_3$ (b), recorded in the range $2\theta = 5°–85°$. The broad signal is caused by a layer of Kapton tape, protecting the sample from the atmosphere during the measurement.

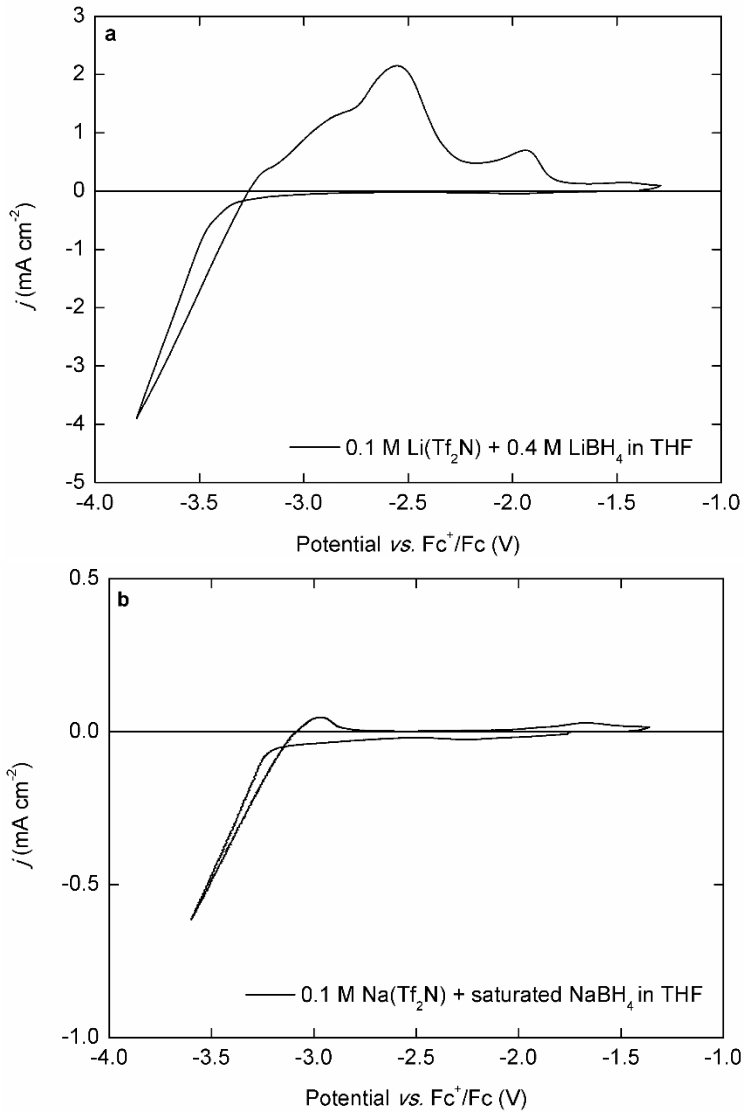

Figure S2. CVs (first cycle) of 0.1 M $Li(Tf_2N)$ + 4 molar equivalents of $LiBH_4$ (a), and 0.1 mol L^{-1} $NaTf_2N$ + saturated $NaBH_4$ (b) in THF, recorded at ambient temperature at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N]. The scan rate was 10 mV s^{-1}.

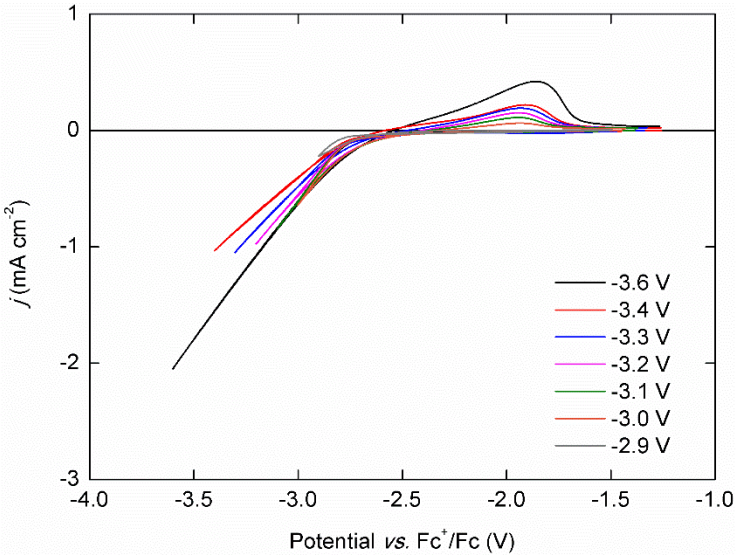

Figure S3. CVs (first cycle) of 0.1 mol L^{-1} $Na[Nd(BH_4)_4](DME)_4$ in THF with varying cathodic vertex potential, recorded at ambient temperature at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in $[BMP][Tf_2N]$.

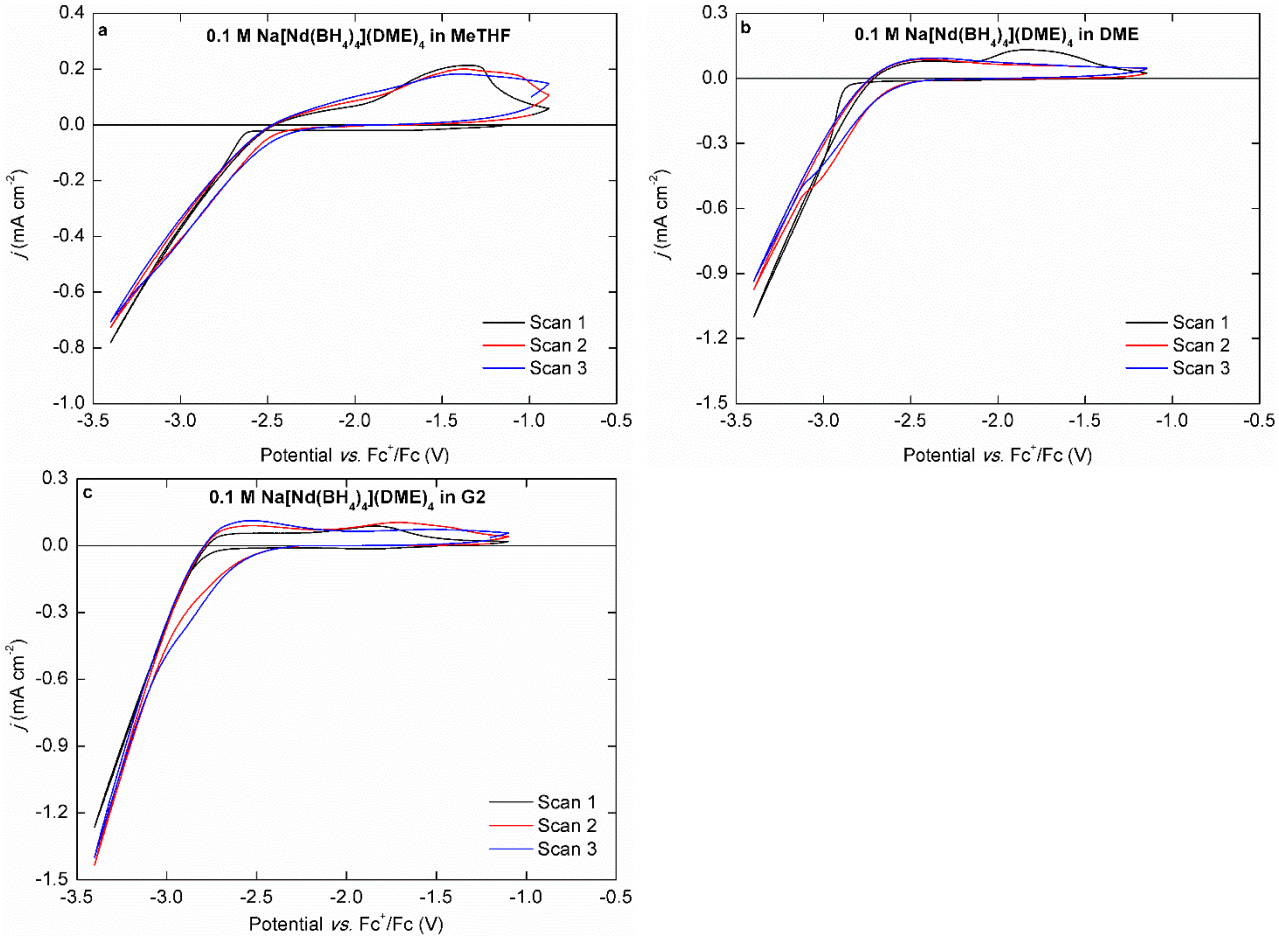

Figure S4. CVs (three scans) of 0.1 mol L^{-1} $Na[Nd(BH_4)_4](DME)_4$ in (a) MeTHF, (b) DME, and (c) G2, recorded at ambient temperature at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N].

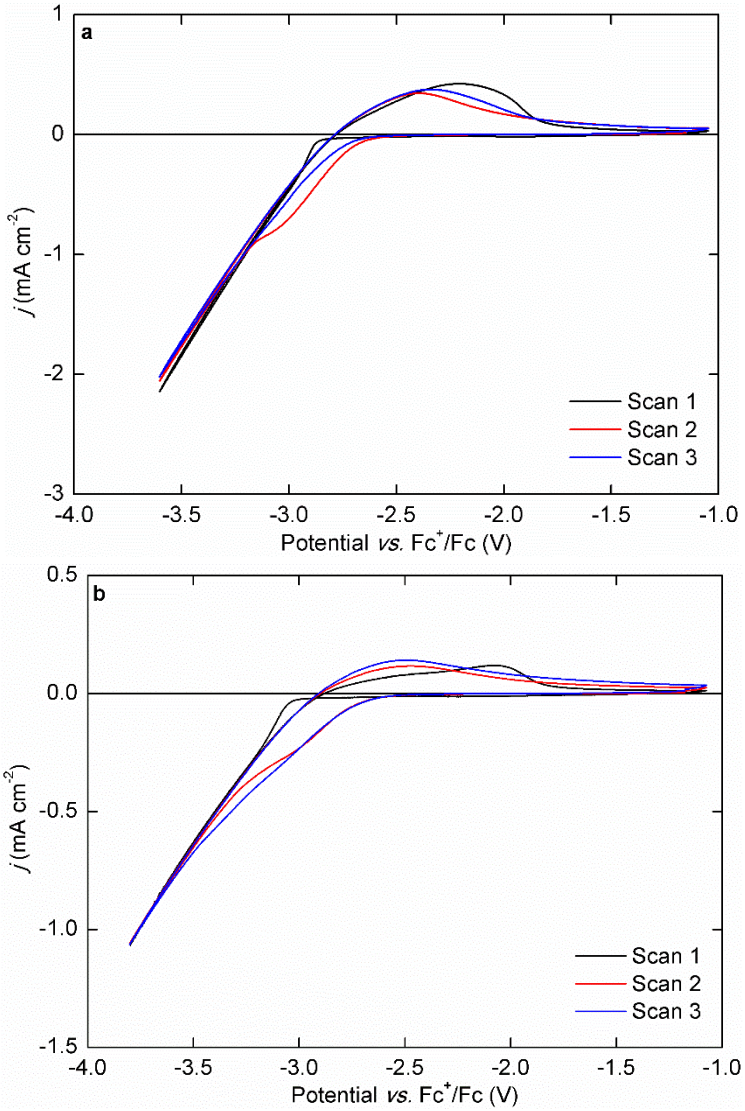

Figure S5. CVs (three scans) of (a) 0.1 mol L^{-1} $Nd(BH_4)_3(THF)_3$ + 0.1 mol L^{-1} $LiBH_4$ in THF, and (b) 0.1 mol L^{-1} $Nd(BH_4)_3(THF)_3$ + 0.1 mol L^{-1} $TBABH_4$ in THF, recorded at ambient temperature at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N].

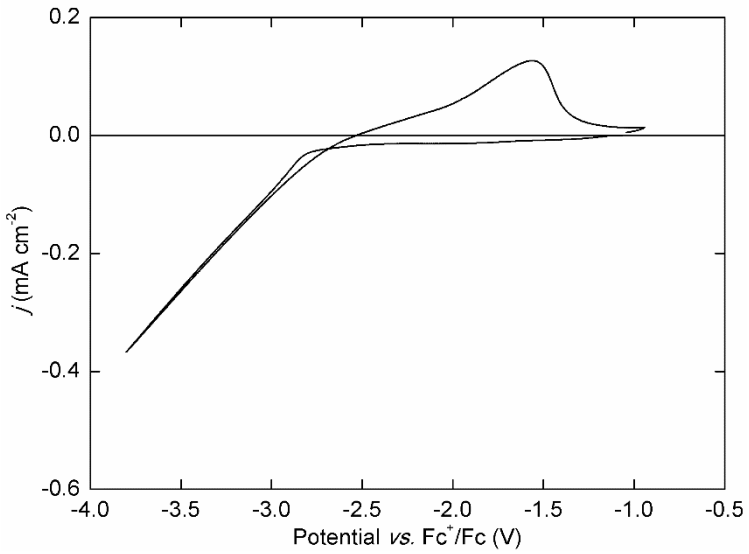

Figure S6. CV of 0.1 mol L^{-1} $Nd(BH_4)_3(THF)_3$ in THF, recorded at ambient temperature at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N].

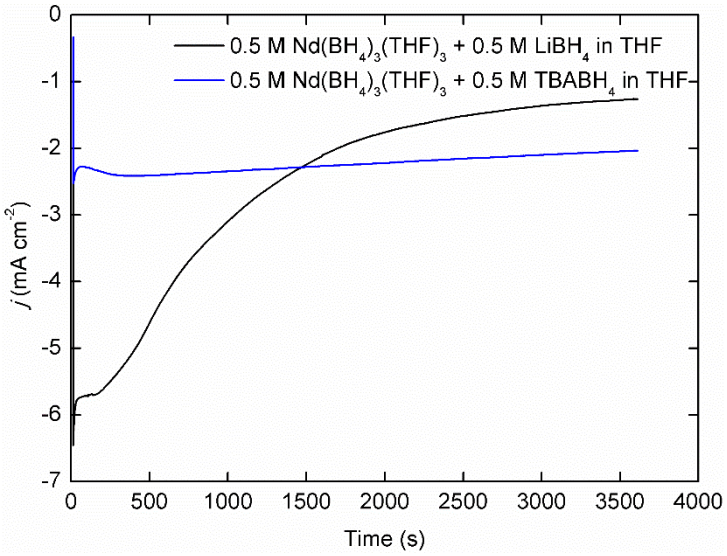

Figure S7. Chronoamperograms recorded at ambient temperature for a potentiostatic deposition at −3.1 V *vs.* Fc^+/Fc for 3600 s in a static solution of 0.5 mol L^{-1} $Nd(BH_4)_3(THF)_3$ + one molar equivalent of $LiBH_4$ in THF (black curve), and at −3.3 V *vs.* Fc^+/Fc for 3600 s in a static solution of 0.5 mol L^{-1} $Nd(BH_4)_3(THF)_3$ + one molar equivalent of $TBABH_4$ in THF (blue curve). The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.3 cm^2 and 1.0 cm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in $[BMP][Tf_2N]$.

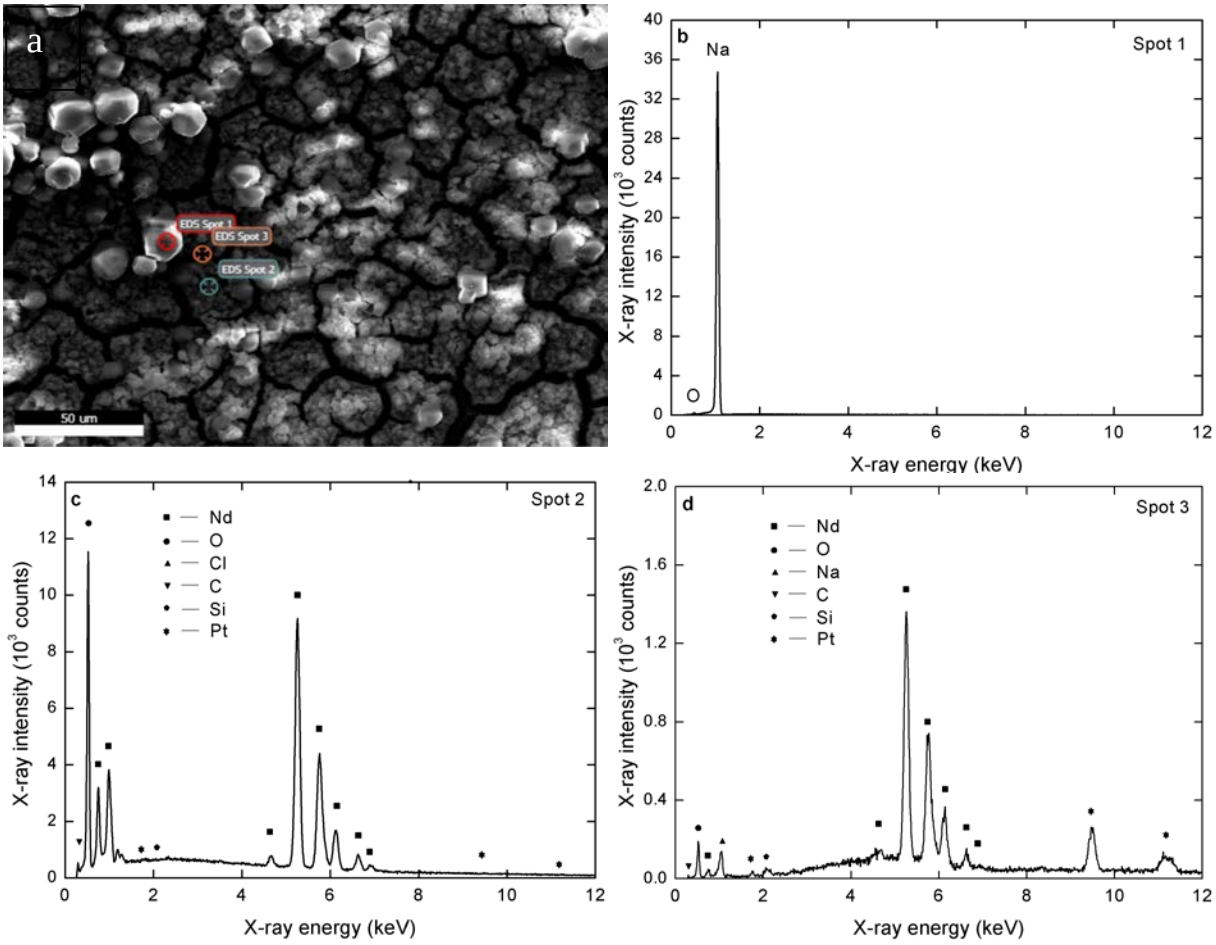

Figure S8. (a) SEM micrograph of a neodymium deposit (theoretical thickness = 2.8 µm) at 500× magnification that was obtained after potentiostatic electrodeposition from 0.1 mol L^{-1} $Na[Nd(BH_4)_4]$ in THF at –3.0 V *vs.* Fc^+/Fc for 2.5 hours. The substrate was a piece of platinum-coated silicon wafer with an approximate surface area of 0.3 cm^2. (b, c, d) EDX spectra in the range 0–12 keV corresponding to the different spots indicated on the SEM micrograph, recorded at an acceleration voltage of 20 kV.

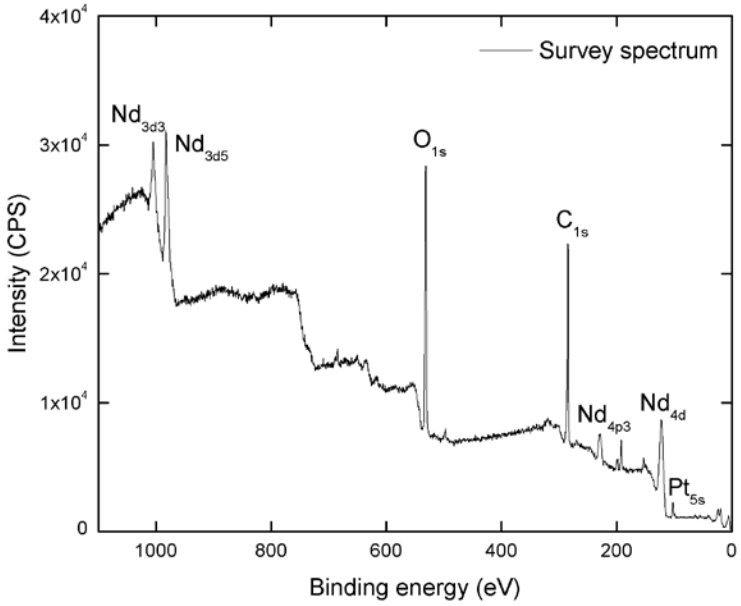

Figure S9. XPS survey scan in the range 0–1100 eV of a neodymium deposit obtained from potentiostatic deposition in 0.1 mol L^{-1} $Na[Nd(BH_4)_4]$ in THF electrolyte at –3.0 V *vs.* Fc^+/Fc for 2.5 hours.